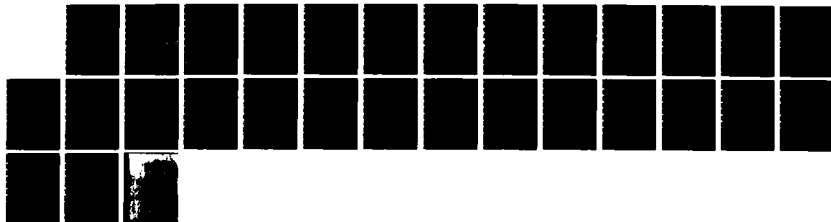AD-A140 947   THEORY AND EXPERIMENTS ON CHEMICAL INSTABILITIES(U)   1/1
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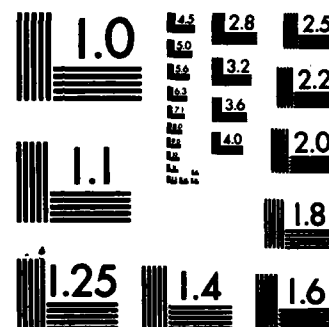   AFOSR-TR-84-0390 AFOSR-81-0125

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Air Force Office of Scientific Research

FINAL TECHNICAL REPORT

Theory and Experiments on Chemical Instabilities
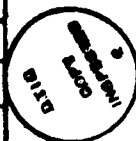
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Research accomplishments are reported in the theoretical and experimental study of chemical instabilities including experiments on macroscopic structure formation in chemical periodic precipitation processes, the theory of periodic precipitation processes, light induced bistability in $S_2O_6F_2$, dynamic fluctuations in optical bistability, dissipation and control in oscillatory reactions, stochastic theory of nonlinear irreversible processes, experiments on chemical waves, and related topics.

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Research Objectives

The objective of this research was the theoretical and experimental study of chemical instabilities including experiments on macroscopic structure formation in chemical periodic precipitation processes, the theory of periodic precipitation processes, light induced bistability in $S_2O_6F_2$, dynamic fluctuations in optical bistability, dissipation and control in oscillatory reactions, stochastic theory of nonlinear irreversible processes, experiments on chemical waves, and related topics.

Summary of Research Accomplishments

There follows a summary of research accomplishments supported in part by the Air Force Office of Scientific Research (and in part by the National Science Foundation).

Experiments on Macroscopic Structure Formation in Chemical Periodic Precipitation Processes

We have carried out an extensive series of experiments on macroscopic structure formation on chemical (colloidal) systems and periodic precipitation processes. Such phenomena have been known for a long time and are frequently called Liesegang rings or band formation.

It had been thought for many years that spatial gradients in concentration or temperature were essential for such band formation but we showed some time ago that macroscopic inhomogeneities may arise in originally uniform colloidal systems. The present series of experiments was focussed on the following issues: (1) What are the properties of Liesegang ring formation as concentrations of initial electrolytes are varied? (2) What is the relation, if any, of the experiments on Liesegang ring formation in the presence of

gradients and in the absence of concentration gradients? (3) In the presence of gradients does nucleation occur only at selected points as predicted by the Ostwald theory, or is the nucleation continuous? (4) What is the meso-scopic structure of the bands formed?

We are first concerned with the temporal and spatial evolution in standard Liesegang experiments in which there exists an initial concentration gradient of electrolytes. We have chosen NH_4OH and $MgSO_4$ to form rings of $Mg(OH)_2$ precipitate in a gelatin gel, as well as KI and $Pb(NO_3)_2$ for periodic precipitation of PbI_2 in an agar gel. A temporal sequence of events during the entire period from the start of a Liesegáng experiment in a test tube to the completion of the final ring pattern has been determined at many locations in the tube by visual observations and by measurements of trans-mitted light, of scattered light, of deflection of the transmitted light beam, and of gravity effects. After diffusion of one electrolyte into the gel medium containing the second electrolyte results in an ion product larger than three times the solubility product, at any and all points in — space we observe the onset of homogeneous nucleation of colloidal par-ticles by a step-like increase of the index of refraction. The colloid concentration and the particle number density at the nucleation site are estimated to be 10^{-2} moles/liter and 10^{15} to 10^{16} cm^{-3}, respectively. Nucleation is followed by the growth of colloidal particles which gives rise to distinct light scattering (turbidity). Both nucleation and colloid formation take place in space continuously; the fronts of these phenomena move through the system and obey a simple diffusion law. A substantial time interval after their passage there arises a localized gradient of the

index of refraction at the prospective ring positions which indicates the
onset of structure formation by means of a focussing mechanism: while the
localized gradient becomes more pronounced and narrower in space, the
turbidity in the regions on either side of the ring location decreases,
which indicates a depletion in colloidal material in the neighboring zones.
Eventually a sharp band of visible precipitate appears, which is clearly
separated from the preceding ring. We conclude that the ring formation is
a post-nucleation phenomenon in that structure arises from a spatially con-
tinuous region of colloid a long time after nucleation has occurred, and
propose that it is associated with the autocatalytic growth of colloidal
particles. The location of rings is not determined by the spatial pattern
of nucleation and colloid deposition as predicted by the Ostwald-Wagner-
Prager theory. Our conclusions are supported by experiments on the influence
of gravity on the ring locations, which provide evidence for the existence
of colloidal particles of several hundred angstroms in size for a substantial
fraction of the time required for the formation of a visible structure. This
work has been published in the Journal of Chemical Physics (172)[†]

We next turn to a systematic investigation of the dependence of the
precipitation patterns on the initial concentrations of reactants. For that
purpose we chose lead nitrate and potassium iodide as the interdiffusing
electrolytes for periodic precipitation in lead iodide in an agar-agar gel.
First we investigate the influence of variation of one of the electrolytes
on the number N, the location x_n and the width Δw_n of bands in test tubes

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[†]The numbers appearing in the text refer to the Publication List on which AFOSR
support is indicated by an asterisk.

placed in the vertical direction. The initial concentration difference $\Delta = \frac{1}{2} [I^-] - [Pb^{++}]$ and the initial ion product $\sigma = [Pb^{++}] [I^-]^2$ are determined to be useful parameters to characterize the variability of the patterns with concentrations, especially when either Δ or σ is small (corresponding to small N). A simple spacing law is obeyed only when σ and Δ are large (N large). There is an influence of gravity on the pattern formation which is excluded in the remaining experiments by simply letting the patterns develop in tubes held in a horizontal position. We measure N, x_n and Δw_n in: (II) experiments in which σ is varied while Δ remains fixed. A broadening of the bands occurs as σ decreases; there is a minimum value σ^* below which no band formation takes place. (III) Experiments in which Δ is varied at constant σ. The location of bands varies with Δ in a complex manner; when Δ is low only one band forms and its distance from the origin increases as Δ approaches zero. For low values of Δ and σ we observe the evolution of zones of colloid of finite width prior to the appearance of one or two sharp bands of precipitate within such zones. (IV) Experiments in which we vary the diameter of the tube ϕ . When ϕ increases beyond 1 cm the bands become broader and more diffuse and the spacing coefficients $p_n = x_{n+1}/x_n$ decrease. The experiments further confirm the instability theory of periodic precipitation processes. This work has been published in the Journal of Physical Chemistry. (178)

In the systematic investigation of periodic precipitation patterns with variation of initial concentrations of reactants we observed two additional phenomena: if the initial concentration difference Δ, or the initial ion product σ, of the reacting electrolytes is small, then (1) there may occur a spatial bifurcation of a single sharp precipitation band into two clearly

separated bands of precipitate as Δ is increased from 0 to a non-zero but small value while σ is kept constant. Both bands are located within a broad zone of low density colloid of lead iodide. We studied the bifurcation by visual observations and measurements of the intensity of transmitted light. (2) The precipitation patterns are found to be increasingly stochastic, in terms of the probability of ring formation and the reproducibility of the location of rings, as either the value of Δ is decreased to zero or the value of σ approaches a lower limit, below which no structure is observed. The experiments on the distribution of ring locations are represented by histograms to which in most, but not all, cases a Gaussian distribution function can be fitted. We also report results on several types of pre-cipitation patterns of electrolyte concentrations. The experiments show the continuous progression of structure formation, from high to zero initial concentration gradients, and thus lead to the suggestion that the origin of pattern formation is the same in all cases. This work has been published in the Journal of Physical Chemistry (181).

We have also investigated the mesoscopic structure of macroscopic inhomogeneities formed in periodic precipitation processes in initially homogeneous colloids, and entirely in the absence of any gradients of con-centrations, temperature or gravitational field effects. The structure is shown to consist of independent colloidal particles and empty regions. Some coagulation of colloidal particles occurs. These observations are again substantiations of the instability theory of periodic precipitation processes. We determined the macroscopic length scale, the average radius of colloidal particles, and the average interparticle distance in the final precipitation patterns and find that these quantities vary strongly with the initial

supersaturation. This work has been published in the Journal of Physical Chemistry (179).

In our experiments on periodic precipitation processes carried out in the last two and a half years we have observed several types of Liesegang patterns which are more complex than the usual concentric rings or parallel bands of precipitates. We have seen radial structures which include reproducible radial gaps, segmentation and irregular complex patterns within concentric rings. Occasionally we have observed the formation of spiral precipitation bands instead of sets of parallel Liesegang bands. These results have been published in SCIENCE in an article entitled "Curiosities in Periodic Precipitation Patterns" (174).

Theory of Periodic Precipitation Processes

We analyze nucleation and colloidal growth in the presence of concentration gradients of electrolytic reactants by means of a postulated set of reaction-diffusion equations , which contain a sink (or reaction) term to account for nucleation and subsequent growth. These equations are more realistic than previous ones used in formulations of the Ostwald hypothesis of Liesegang ring formation, in which that formation is supposed to be a pre-nucleation process, but in limits contain the previous formulations. We calculate length and time scales of our equations and estimate values of the physical quantities involved. Numerical solutions of our equations predict nucleation to occur as a spatially continuous process, in agreement with experiments. In previous formulations spatial discontinuities in nucleation were obtained by unwarranted approximation or ad hoc assumptions (boundary conditions). This work has been published in the Journal of Chemical Physics (176).

We have also investigated the instability theory of spatial pattern formation in precipitating systems which focusses on post-nucleation phenomena in contrast to the supersaturation (pre-nucleation) theory of W. Ostwald. A scale analysis shows that very slow particle growth kinetics are necessary to match the experimental observations; this result rules out diffusion-limited growth of colloidal particles. We further show that colloidal particle diffusion is quantitatively unimportant for the process of structure formation and does not provide a macroscopic length scale for diffusion-limited growth kinetics. This work has been published in the Journal of Chemical Physics (177).

The temporal evolution of first order phase transition is a process with three frequently nearly separate stages. The first is nucleation with a new phase as formed out of the metastable old phase (if there is no free energy barrier to nucleation, phase separation occurs by a process called spinoidal decomposition). Nucleation usually yields a large number of particles with a narrow distribution of particle sizes. In the next stage the nuclei grow rapidly at the expense of the old phase. In the final stage, known as Ostwald ripening, the new phase evolves so as to minimize its surface free energy. During that final stage there is a drastic reduction in a number of particles of the new phase by many orders of magnitude. We have studied this last stage of phase separation and have presented a new derivation of the kinetics of that stage of Ostwald ripening. We use a multiple time scaling technique and derive the power laws of the time dependencies for the distribution function of the particles size of the new phase. We also present correction terms to first-order treatment. The derivation clarifies and corrects prior work. This research has been published in the Journal of Chemical Physics (184).

Light Induced Bistability in $S_2O_6F_2$.

Bistability is predicted and experimentally verified in an illuminated, gas phase reaction mixture of peroxydisulfuryl difluoride and fluorosulfate free radicals. The steady state solutions of simple dynamical equations, based on the assumption of spatial uniformity, are in good agreement with hysteretic effects observed in bulk absorption measurements: sharp transitions between stable branches of different absorption occur as the laser power used to irradiate the system is slowly varied. The appearance of a "flame", previously reported by others and noted here, is explained by an extension of the model which enables calculation of spatial inhomogeneities. The results of the extended model, when bulk averaged, are similar to those for the uniform system; however, large scale structure and steep gradients, corresponding to a "flame", are predicted in the case of high absorption, with corresponding high fluorescence. Experimental measurements of fluorescence profiles confirm these predictions. A critique is made of prior work on bistability in the N_2O_4/NO_2 system. Hysteresis was observed in that system but is now believed to have been due to critical slowing down near and above the critical temperature for onset of bistability rather than below that temperature.

Dynamic Fluctuations and Optical Bistability

We present results on the time correlation function of a system undergoing absorptive optical bistability. We first use the Zwanzig-Mori formalism to calculate time correlation functions both near marginal stability points and in the coexistence region. Near marginal stability points the th͏ͮ p dicts large deviations from a single exponential

form of the correlation function. The truncated continued fraction expansion is shown to become inapplicable close to the coexistence point. The difficulties are due to the presence of long time scales, viz. the very large mean first passage times between the two metastable steady states. When these scales are important we show that the memory kernel relaxation is no longer faster than that of a field fluctuation. An increase in the size of the system increases the disparity of the time scales and thus exacerbates the problems of the projection operator formalism.

We next present an ansatz for the correlation function incorporating the four major time scales important near coexistence, the two single branch relaxation times and the two mean first passage times for transitions between the stable states. This form of the correlation function avoids the difficulties cited in connection with the use of the projection operator method. This work has been published in Z. f. Physik (165).

Dissipation and Control in Oscillatory Reactions

We have studied the issues of dissipation and control in autonomous oscillatory reactions in externally perturbed chemical reactions and in oscillatory chemical engines such as glycolysis.

We began with a theoretical and chemical analysis of the problem of an oscillatory chemical reaction driven by varying concentrations of reactants externally in a periodic manner. We use for this purpose two models, the Selkov and the Higgins models, amended to include reverse reactions. This apparently modest extension of the model as previously used introduces enormous enrichment in the type of behavior, including hysteresis, excitability, oscillations, and a variety of multiple stationary states. We calculate the dissipa-

tion, that is the rate of entropy production, in order to ascertain variations in that quantity with variations in frequency of the external perturbations of concentrations of reactants. We find, as in previous studies, resonance effects in entrainment bands. The resonance asserts itself as a maximum in the amplitude of the response in concentrations of chemical species of the oscillatory system to the external perturbation and entrainment bands occur at frequencies of external perturbations which are either the same or simple sub-multiples of the natural frequency of the oscillatory chemical system. A variety of interesting control features appear. The occurrence of oscillations is linked to a high differential susceptibility of the steady state flux with respect to changes in overall affinity. When both chemical reactants and products of the reactions are varied sinusoidally then appreciable changes in the dissipation of the total reaction may be obtained. The sign of the change depends on the relative phase between input and output oscillations. Small phase changes may lead to a large change in dissipation which may be used as an additional control feature. A phase change can also alter the mode of operation from periodic to quasi-periodic with attendant changes in dissipation. A part of this work has been published in the Journal of Chemical Physics (160) and the remainder in Progress of Theoretical Physics (167).

The occurrence of entrainment bands in oscillatory systems perturbed by periodic external concentration changes provides a technique for obtaining clues about the complex reaction mechanism of oscillatory reactions. The location of entrainment bands is difficult to determine and we have therefore proceeded to a mathematical analysis of that question. Progress is possible based on prior work by Loud and Bushard.

Experiments have been reported on the effect of varying the concentrations of an initial reactant externally in oscillatory reactions. Periodic perturbation of oscillatory reactions gives rise to several interesting phenomena. (1) Entrainment of the limit cycle occurs at certain frequencies of the external perturbation. In a range of frequencies of the perturbation near the natural frequency of the limit cycle there exists the fundamental entrainment band in which the limit cycle follows the external perturbation. (2) In entrainment bands there occur resonance effects in the amplitude of the oscillations of the chemical intermediates and in functions of the concentrations, such as the dissipation. (3) Within entrainment bands the phase difference between the periodic perturbation and the periodic variation in concentration of a given species is fixed, which is called "phase locking". The phase difference generally is not the same for all the chemical intermediates in the mechanism. (4) Outside of entrainment bands the response of the system to external perturbations produces quasi-periodic or chaotic variations of concentrations in time. The transition from entrained, periodic variation to quasi-periodic variation is analogous in some ways to a phase transition; for instance, there occurs critical slowing-down so that the decay of transients becomes very long.

The study of these phenomena, of interest in themselves in kinetics and in many other areas in physics and engineering, provides insight into reaction mechanisms but experiments and numerical analysis are severely hindered in the determination of the entrainment regions by the existence of critical slowing-down; both methods take inordinate times near the edges of entrainment bands. Hence it is important to have mathematical techniques for obtaining widths of entrainment regions and phase differences for an assumed chemical reaction mechanism in order to assess the utility of that mechanism in comparison with

readily available experiments on entrainment (not near the edges of the band) and on phase-locking.

Periodic perturbations of a chemical species in a reaction mechanism are probes for the study of the rates and mechanisms of that reaction. This approach has been a great success for reactions close to equilibrium and similar techniques may be useful for reactions far from equilibrium. We have begun a study of the theory of homogeneous oscillating chemical systems subject to small and large periodic perturbations. By applications of theorems of Wasow and Levinson we generate for arbitrary perturbations and several model systems approximate solutions in terms of the rate coefficients for the time-dependent trajectories and thereby obtain relaxation rates and phase relationships between concentrations of the various species and the perturbation. For sufficiently large amplitudes of perturbation, the chemical system always responds with a stable periodic solution with the same frequency as the perturbation. The approximate analytic results compare well with the numerical solution of the Sel'kov model subjected to large perturbations. Using theorems by Loud and Bushard, we show for periodic perturbations of small amplitude the existence, stability, and widths of large numbers of entrainment bands. The relative widths of entrainment bands are approximated formally, and nearly all, other than for fundamental entrainment, are unobservable numerically or experimentally. An oscillating chemical system can be perturbed with a single perturbation to generate arbitrary numbers of periodic attractors. Our prescription is applied to find a perturbation which produces two periodic attractors in the Sel'kov model. The analysis is confirmed by numerical simulation. This work has been published in the Journal of Chemical Physics (182).

We have studied the kinetics of the hydration of 2,3-epoxy-1-propanol to glycerine in a continuous stirred tank reactor. The agreement between our numerical and analytical results and others' experimental measurements is extremely good for the autonomous system; we predict and then verify numerically the existence of normal and inverted Hopf bifurcations. We then periodically perturb the system to obtain details of entrainment: Entrainment bandwidths, phase locking, and resonance in the amplitudes of temperature and concentrations. We also numerically calculate the dissipation and find, at fixed chemical flux, conversion rate, and average output temperature, that the total dissipation is unchanged under resonance conditions; the dissipated energy, however, can be varied among the different heat baths and free energy sinks by varying the perturbation frequency. Thus we establish the interesting possibility of <u>distribution</u> <u>of</u> <u>dissipation</u> by means of external perturbations. This work has been published in the Journal of Chemical Physics (183).

We have made a detailed theoretical study of glycolysis which is the conversion of glucose and ADP, a low energy species, into pyruvate or lactic acid and ATP, a high energy species which is the universal energy coinage in living systems. The purpose of this work was the investigation of control features in that reaction and an analysis of the efficiency of energy transduction. There are two sub-oscillatory mechanisms in the overall reaction, the first being the phosphofructo-kinase (PFK) reaction and the second being the pyruvate kinase (PK) reaction. On the basis of a reaction mechanism established with the best experimental evidence available, we find that the PK sub-oscillatory system is driven by the primary oscillophor. Under oscillatory conditions the average ATP/ADP ratio is increased substantially over non-oscillatory steady state conditions. That implies that the Gibbs free energy transduction under oscillatory conditions is higher than under

steady state conditions and hence under oscillatory conditions the dissipation is reduced. This increase in efficiency occurs because the primary oscillophor operates at a frequency which elicits a resonance response in the second oscillophor, the PK reaction. The resonance is no accident: the PK reaction tunes the primary oscillo-phor (PFK) to its own resonance frequency. On the basis of this work we have suggested that oscillatory biological reactions (of which more than 250 are known to date) have developed in evolution due to an increased efficiency in energy trans-duction obtained thereby. Furthermore, a number of interesting control features arise including a high throughput susceptibility for small changes in Gibbs free energy difference of reactants and products; changes in dissipation made possible by phase shifts of one chemical intermedicate in relation to another in the oscillatory operation; and the possibility of variable dissipation dependent on the overall frequency of the oscillatory reaction mechanism. This work has been published in a number of articles in Science (158), Biophysical Chemistry (159), and in the Proceedings of the National Academy (161, 162, 175).

Stochastic Theory of Nonlinear, Irreversible Processes.

The description of a system beyond that of deterministic equations for averages of physical quantities requires consideration of fluctuations. Such fluctuations are frequently described by Langevin or Fokker-Planck equations. We have studied the solution of such stochastic equations by finding path integrals which are functional integrals weighted according to the time integral of a thermodynamic Lagrangian along the path. We prove that the thermodynamic Lagrangian is unique for single or multi-variable processes in flat spaces, contrary to earlier statements that the Lagrangian depends on an arbitrary parameter (α). We further show that the choice of parameter α is equivalent to the choice of a stochastic calculus: $\alpha = 0$ corresponds to

the Ito calculus and $\alpha = \frac{1}{2}$ to the Stratonovich calculus. Once the calculus

has been chosen, consistent thermodynamic Lagrangians are derived by follow-

ing the rules of that calculus. From the thermodynamic Lagrangian we obtain

the equations describing the most probable path of the system. When Laplace's

method can be used to approximate the path integral, the conditional propa-

gator can be written as a product of a thermodynamic factor and the kinetic

factor. The thermodynamic factor is large if a process is thermodynamically

favorable, but the kinetic factor may be small if large changes in the sto-

chastic variables are required on a short time scale. This work has been

published in the Journal of Chemical Physics (163) and a follow-up article

on path integral solutions of the Fokker-Planck equation for a system with

nonconservative forces has been published in Physics Letters (166).

When the conditional propagator for a single-variable Fokker-Planck equation

is represented in functional path integral form, it separates into a path-

independent thermodynamic factor and a reversible, time-dependent kinetic factor.

The validity of the Onsager-Machlup-Laplace (OML) approximation to the conditional

propagator is determined solely by the mechanical potential associated with the

kinetic factor. The OML approximation is exact if the underlying mechanical

force is linear; Hongler's model exemplifies a class of nonlinear Fokker-Planck

equations that are solved exactly by the OML approximation, because the nonlinearity

is confined to the thermodynamic factor. Contrary to earlier suggestions, neither

the existence of turning points in the mean paths nor limited information content

of the path of least thermodynamic action indicates the breakdown of the OML

approximation. When classical paths on the mechanical potential surface coalesce,

however, the OML approximation breaks down catastrophically. Divergences

analogous to the classical catastrophes of scattering theory are found for extremal

path durations; these extremal times must exist whenever the underlying mechanical potential surface possesses two or more nonidentical maxima. Path coalescence and the consequent divergence of the OML approximation is illustrated for a system with the deterministic kinetics of the Schlögl model and constant probability diffusion coefficient. Catastrophic divergences of the OML approximation may be predicted and classified by generalization of similar problems found in the stationary phase approximation of semiclassical scattering theory; additionally, methods of semiclassical collision theory suggest approaches for eliminating erroneous divergences of the conditional propagator for nonequilibrium thermodynamic systems. This work has been accepted for publication in the Journal of Chemical Physics. (186)

Experiments on Chemical Waves

We have performed experiments on chemical waves in the Belusov-Zhabotinski reaction. Measurements were made by means of absorption of a weak laser beam and the extent of absorption was determined by an optical multichannel analyzer, a vidicon system, at a given instant of time. The instrument records the absorption on 500 photo-sensitive spots to a resolution of about 0.1 mm. These measurements are the first quantitative recordings of properties of chemical waves other than by inspection by eye. Our preliminary results show an oscillatory behavior in the amplitude of the wave as well as an oscillatory component in the velocity of the wave. The vidicon readings are transmitted to a Minc computation system and displayed on a screen in real time. Experiments are in progress on measurements of the wave profile and wave velocity and their variations with changes in initial concentrations of reactants.

Photodissociation of I_2.

We have constructed and completed an experimental system for measurements on photo-dissociation of I_2. Under illumination of a given intensity of light from an argon ion laser, the reaction $I_2 + H\nu = 2I$ reaches a steady state at a given temperature. This system has only a single stationary state but upon perturbation the reaction is predicted to return to the steady state in an oscillatory way. After a series of measurements it appears that the rate coefficients and thermal conduction coefficients in the system are such that the oscillatory return to the steady state is excessively damped and likely to be unobservable. In the study of this system we also attempted to measure the recombination rate of three iodine atoms to form $I_2 + I$.

Critique of a proposed stability criterion for chemical systems far from equilibrium.

Noyes (Noyes, R.M. (1981) Proc. Natl. Acad. Sci. USA 78, 7248) has obtained a result for the Gibbs free energy per unit mass in a continuous flow stirred tank reactor, which states that the steady-state free energy increases monotonically with decreasing residence time for any stable stationary point. We show that his derivation is based on an erroneous stability criterion. We further investigate the dependence of the Gibbs free energy on residence time for the case of mass-action kinetics and ideal mixtures. We then apply this development to Schlögl's trimolecular reaction mechanism (Schlögl, F. (1971) Z. Phys. 248, 446-458) and show that Noyes' conjecture is violated for this simple example. This work has been published in the Proceedings of the National Academy of Sciences (185).

Multiple Ranges of Flowrate with Bistability.

Continuous flow stirred tank reactor (CSTR) conditions are imposed upon Schlögl' trimolecular reaction mechanism $A + 2X \rightleftharpoons 3X$ and $X \rightleftharpoons B$. A nonzero constant

flow rate (= inverse residence time) rather than constant concentrations of A,B forces the system far away from equilibrium. This change in constraints leads to some surprisingly complex features; first the system has bistability for separate ranges of flow rates, under constraints of all other parameters being fixed including the concentration of the chemical species in the input. This phenomena occurs even if the input contains A alone. Secondly, there occur limit cycle oscillations but in that case the input has to include B or X as well as A. This work has been accepted for publication in The Journal of Chemical Physics.

Thermodynamic Processes, Time Scales and Entropy Production

We analyze time-dependent processes in thermodynamic systems by obtaining the entropy production in terms of the relaxation times of these processes. The various possible limits of these times and their ratios lead to a classification into reversible, both quasistatic and otherwise, and irreversible processes. In one of these limits, it is possible for a reversible process not to be quasistatic, but this limit is physically not interesting. For the case of heat conduction, that limit requires infinite thermal conductivity, $\alpha \to \infty$, such that the flow of heat is not zero as $T \to T_{ex}$. As an application, we compare the efficiency and power output of a Carnot cycle defined with nonquasistatic reversible branches and that of an irreversible Carnot cycle. This work has been published in the Journal of Physical Chemistry (173).

Treatments of Symmetry Rules in Chemical Reactions.

We compare a recently presented approach to the determination of symmetry rules for chemical reactions based on adiabatic electronic states to earlier work in which a quasiadiabatic representation was used. The adiabatic approach is shown not to lead directly to Woodward-Hoffmann symmetry rules, and a number of the conclusions of the adiabatic work are shown to be incorrect and inconsistent. An indirect approach for deriving the Woodward-Hoffmann rules in the adiabatic representation is presented which uses the connection between the adiabatic and

quasiadiabatic representations to relate barrier height to the quasiadiabatic electronic matrix element. This work has been accepted for publication in the Journal of Chemical Physics.

Publications

160. "Dissipation in an oscillatory reaction mechanism with periodic input," J. Chem. Phys. 74, 2339 (1981). (with Yves Termonia)

161. Oscillations and Control features in glycolysis: Numerical analysis of a comprehensive model," PNAS 78, 2952 (1981). (with Yves Termonia)

162. "Oscillations and control features in glycolysis: Analysis of resonance effects," PNAS 78, 3563 (1981). (with Yves Termonia).

*163. "Path integral solutions of stochastic equations for nonlinear irreversible processes: The uniqueness of the thermodynamic Lagrangian," J. Chem. Phys. 75, 976 (1981). (with Katharine L. C. Hunt).

164. "Two topics in chemical instabilities: I. Periodic precipitation processes. II. Resonances in oscillatory reactions and glycolysis. Springer Ser. Synergetics, 12, 180-5 (1981).

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*166. "On the Path Integral Solution of the Fokker-Planck Equation for a System with Non-conservative Forces," Phys. Lett. 84A, 465 (1981); (with Frederick W. Wiegel).

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168. "On the efficiency of thermal engines with power output: Consideration of inertial effects." J. Chem. Phys. 75, 5485 (1981). (with Victor Fairen).

169. "On the efficiency of thermal engines with power output: Harmonically driven engines," J. Chem. Phys. 75, 5490 (1981). (with Victor Fairen).

170. "Dissipation in driven oscillatory chemical systems with applications to glycolysis," Kinam Revista de Fisica 3, 173 (1981). (with Paul Rehmus and Yves Termonia).

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*172. "Measurements of temporal and spatial sequences of events in periodic precipitation processes," J. Chem. Phys. 76, 1392 (1982) (with Shoichi Kai and Stefan C. Müller).

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174. "Curiosities in Periodic Precipitation Patterns," SCI 216, 635 (1982) (with Stefan C. Muller and Shoichi Kai).

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*176. "Nucleation and colloidal growth in concentration gradients (Liesegang rings)" J. Chem. Phys. 77, 1302 (1982) (with Gerd Venzl).

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*183. "The periodically forced conversion of 2,3-epoxy-1-propanol to glycerine: A theoretical analysis," J.Chem.Phys.78, 7241 (1983) with Paul Rehmus, E.C. Zimmermann and H.L. Frisch.

*184. "Kinetics of phase transitions: Theory of Ostwald ripening," J. Chem. Phys. 79, 373 (1983) (with J.A. Marqusee)

*185. "Critique of a proposed stability criterion for chemical systems far from equilibrium," Proc. Natl. Acad. Sci. USA 80, 3133 (1983). (With Claus Escher)

*186. "Comments on two treatments of symmetry rules in chemical reactions," J.Chem.Phys. $\underline{79}$, 2854 (1983). (with Horia Metiu and George C. Schatz).

*187. "Path integral solutions for Fokker-Planck conditional propagators in nonequilibrium systems; Catastrophic divergences of the Onsager-Machlup-Laplace approximation," J. Chem. Phys. $\underline{79}$, 3765 (1983). (with Paul M. Hunt and Katharine L.C. Hunt).

*188. "Multiple ranges of flow rate with bistability and limit cycles for Schlögl's mechanism in a CSTR," J.Chem.Phys. $\underline{79}$, 3773 (1983). (with Claus Escher).

*189. "Commentary: Dissipation Regulation in Oscillatory Reactions - Application to Glycolysis," Aspects of Chemical Evolution, Proceedings of the XVIIth Solvay Conf. on Chem., Edited by G. Nicolis, Wiley, N.Y. (1983) (with Peter Richter).

*190. "Theory of Ostwald ripening: Competitive growth and its dependence on volume fraction," J. Chem. Phys. $\underline{80}$, 536 (1984). (with J. A. Marqusee).

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*191. "Light induced bistability in $S_2O_6F_2 \rightleftharpoons 2SO_3F$: Theory and experiment," J.Chem. Phys. __, ____ (1984). (with E. C. Zimmermann).

192. "Generation of Multiple Attractors and Nonequilibrium Phase Transitions," J. Chem. Phys. __, ____ (1984) (with Paul Rehmus and William Vance).

193. "Periodically Perturbed Chemical Systems," in Oscillations and Travelling Waves in Chemical Systems, Editors Richard J. Field and Maria Burger, John Wiley & Sons, N.Y. (1984) (with Paul Rehmus).

194. "Marginalia on the Evolution of Chemistry," Rehovot __, ____ (1984).

List of Professional Personnel

Postdoctoral Affiliates

Michael Delle Donne (9/15/78 - 12/31/80)

Escher, Claus (1/26/82 - 7/31/83)
    Now at the Institut fur Theoretische Physik
            D5100 Aachen, W. Germany

Fairen, Victor (10/15/79 - 10/31/81)
    Now at Universidad de Valladolid
            Valladolid, Spain

Hatlee, Michael D. (8/25/80 - 7/16/82)
    Now at the University of Missouri
            Kansas City, missouri 64110

Kai, Shoichi (11/8/79 - 8/28/81)
    Now at the Kyushu Inst. of Technology
            Tobata, Kitakyushu 804, Japan

Marqusee, Jeffrey A. (10/1/81 - 8/31/83)
    Now at Univ of California, San Francisco
            San Francisco, California 94143

Müller, Stefan E. C. (2/23/79 - 9/26/79)
    Now at Max Planck Institut fur Ernahrungsphysiologie
            D4600 Dortmund 1, West Germany

Rehmus, Paul (10/16/79 - 1/31/83)
    Now at The Rand Corporation
            1700 Main St., Santa Monica, CA 90406

Richter, Peter (11/1//77 - 10/31/80)
    Now at the Universitat Bremen
            28 Bremen 33, W. Germany

Termonia, Yves (8/1/79 - 11/15/81)
    Now at the Weizmann Institute of Science
            Rehovot, Israel

Venzl, Gerd (8/22/80 - 10/31/81)
    Now at the Technische Universitat Munchen
            8046 Garching, W. Germany

Visiting Faculty

Hunt, Katharine Clarke (summers 1981,1982,1983)
    Professor at Michigan State University
            East Lansing, Michigan 48823

Hunt, Paul (summers 1981, 1982, 1983)
    Professor, Michigan State University
            East Lansing, Michigan 48823

Student Personnel

Kramer, Jesse (5/1/80 -)

Wood, Peggy Marie (3/4/80 -)

Zimmermann, Edwin C. (7/1/80 -)

Interactions

Invited papers were presented at the following institutions and conferences:
1981

Jan. 8   X Reunion de Fisica Estadistica, Cocoyoc, Mexico, Resonances and Control Features

Feb. 13   Michigan State University, Invited Lecture, Glycolysis

Feb. 20   Los Alamos Laboratory, Discussions and Site Visit, Efficiency

Feb. 27   University of New Orleans, Distinguished Lecture Series, Efficiency

Mar. 30   University of California, San Diego, Energy Center, Invited Lecture

Apr. 20   University of Chicago, Invited Lecture, Efficiency, Glycolysis

Apr. 22   University of Notre Dame, Reilly Lectureship, series of three lectures: 1) Instabilities, 2) Periodic Precipitation, 3) Glycolysis

Apr. 28   National Academy of Sciences, Invited Lecture, Glycolysis, Biochemical Systems

May 31   Arizona Science Forum, Phoenix, Invited Lecture, "The Impact of the Weizmann Institute on Sciences ...."

June 6   Los Angeles, Weizmann Institute of Science International Leadership Conference, Lecture

July 25 to 30   Gordon Conference, Invited Lecture, Discussion Leader, Thermodynamics

Sept. 2,3   Raychem, Swinden, England, Chemical Instabilities, Oscillations, Glycolysis

		Glycolysis, Per. P. Proc.
Sept. 5	Cambridge Univer,	
Sept. 10	International Conference, Bordeaux	" "
Sept. 14	Max Planck Institut, Dortmund	" "
Sept. 16	Theoret. Phys., Aachen	" "
Sept. 17	Chemical Physics, Brussels	" "
Sept. 21	University of Leiden	" "
Sept. 24	University of Bremen	" "
Sept. 29	Max Planck Institut, Göttingen	" "

Oct. 7   American Institute of Aeronautics and Astronautics, Invited Remarks, Palo Alto, CA

1982

Feb. 25,26   Industrial Affiliates Program
Hydrodynamic and Chemical Instabilities
1. Arranged program with Bud Homsey
2. Presented lecture on Resonances and Periodic Precipitation Processes

Apr. 26-30   Lecture at Bell Research Laboratories ⎫ Periodic Precipitation
                      Allied Chemical Corp. ⎬ Processes
                      Exxon ⎭ Glycolysis

May 26   Lecture at IBM, San Jose

July 25   Gordon Conference on Chemical Instabilities, Invited Lecture, Periodic Precipitation Processes

Sept 13   ACS Symposium on Instabilities, Chairman, Lecture
      29   University of Illinois, Chemical Instabilities

Dec. 1-3   AFOSR, Colorado Springs, Periodic Precipitation Processes

1983

Mar 15	NATO Meeting at Austin Texas, Periodic Precipitation Processes
Mar 28	Am. Chem. Soc. National Meeting, Invited Lecture, Thermal and Chemical Engines
Apr 25	Argonne National Laboratory, Conference on Engineering (DOE) Chemical Nonlinear Engines
May 5	Los Alamos, "Fronts, Patterns ...", Liesegang Rings
May 24	AAAS Meeting, Detroit, Periodic Precipitation Processes
Jun 15	57th Colloid and Surface Science Mtg (ACS), Toronto, Invited Lecture: Periodic Precipitation Processes
Jun 27	Rhone-Pouenc (Paris), Chemical Instabilities
July 5	Technical University, Munich, Chemical Instabilities
Aug 10	Los Alamos, Invited Lecture, Engines
Oct 10	Univ of Chicago, Hudnall Lecture, Periodic Precipitation Processes
Oct 12	U.S. Coast Guard Academy, Chemical Instabilities
Oct.26	Queens College, Chemical Instabilities
Nov 4	Appl. Math. Dept., Stanford, Engines - Chem. Therm. Biol.
Nov. 16	Chem. Engineering, Stanford, Engines - Chem. Therm. Biol.

Research discussions were held at Hanscom Field, Bedford, Massachusetts With Drs. Edward Kenneally and Russell Armstrong on Chemical and Hydrodynamic Instabilities in the Upper Atmosphere.

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